

High Pressure-High Temperature Investigations of the stability of Nitride Spinel in the System $\text{Si}_3\text{N}_4 - \text{Ge}_3\text{N}_4$

E. Soignard, P. McMillan (University College, London), M. Somayazulu, O. Sankey (Arizona State U.), H-K Mao (Geophysical Lab.), and J-J Dong (Auburn U.)

Soig1004

Beamline(s): X17B1

Introduction: Dense nitride compounds are known to provide important technological materials, including refractory ceramics, superhard materials and wide gap semiconductors¹. Despite major advances over the past ten years, the solid-state chemistry of nitride compounds remains less well developed than that of oxides. In particular, little is known about nitride compounds that might exist at high P,T conditions. Based upon the extensive polymorphism known to exist among oxides, it is likely that a rich solid-state chemistry awaits discovery². Since nitrides are generally more covalent than, the new materials are likely to have lower compressibility, higher hardness and narrower bandgaps. In the last year itself, different groups reported the first three examples of nitride spinel compounds, i.e., $\gamma\text{-Si}_3\text{N}_4$, $\gamma\text{-Ge}_3\text{N}_4$ and $\gamma\text{-Sn}_3\text{N}_4$ ³⁻⁵.

Methods and Materials: Laser heating at high pressure has been used to synthesize the spinels of Si_3N_4 and Ge_3N_4 from their low-pressure forms (α or β forms). A multi-mode Nd:YAG laser was used to heat the samples to temperatures in excess of 2000 K at pressures above 20 GPa to drive the sample into the stability field of the spinel. Five different compositions of the mixture $\text{Ge}_3\text{N}_4\text{-Si}_3\text{N}_4$ were used as starting materials with N_2 as pressure medium. *In-situ* energy dispersive x-ray diffraction patterns were recorded while heating the samples at high pressures to monitor the reactions. For all starting compositions, the final product consisted of a spinel having a composition close to $\gamma\text{-Ge}_3\text{N}_4$ and a new phase.

Conclusions: Laser heating the mixtures of the two nitrides Si_3N_4 and Ge_3N_4 at pressures of the order of 20 GPa led to the synthesis of the new nitride spinel phase GeSi_2N_4 . This is the first synthesis of a ternary nitride spinel. The result is evidence for the existence of a *solvus* in the system $\gamma\text{-Si}_3\text{N}_4$ - $\gamma\text{-Ge}_3\text{N}_4$.

Acknowledgments: The authors thank the NSF-ASU MRSEC (grant No. DMR-96-32635) for support.

References: ¹R. Niewa and F. DiSalvo, Chem. Mater., 10, 2733 (1998); ²W. Schnick, Angew. Chem. Intl. Ed., 38, 3309 (1999); ³A. Zerr *et al*, Nature, 400, 340 (1999); ⁴K. Leinenweber *et al*, Chem-Eur. J., 5, 3076 (1999); ⁵N. Scotti *et al*, Z. Anorg. Allg. Chem., 625, 1435 (1999).

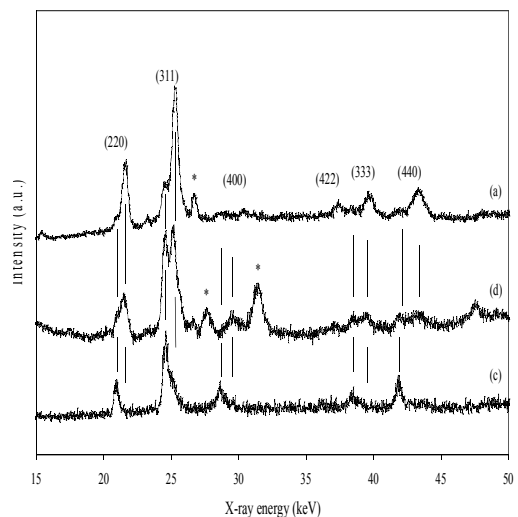


Figure 1. EDXD patterns at $12.005(2)\text{\AA}$ for three compositions of $\alpha\text{-Si}_3\text{N}_4 - \beta\text{-Ge}_3\text{N}_4$ at 20 GPa in the ratio (a) 2:1; (b) 1:1 and (c) 1:2. All the peaks due the spinel phase formed at high temperatures are split.